

DESCRIPTIONPARTICLES FOR DETERGENT ADDITION5 TECHNICAL FIELD

The present invention relates to detergent additive particles, composite detergent particles and a granular detergent composition.

BACKGROUND ART

10 Recently, as laundry detergents, granular detergent compositions (compact detergents) have been the main trend. The granular detergent composition has been prepared by using various techniques such as mixing, granulation, compression and pulverization, and has brought about great merits in the convenience upon use, reduction of transportation costs, and the like. On  
15 the other hand, the granular detergent composition tends to have poorer solubility as compared to a low-bulk density detergent. Especially in the dispenser (detergent supplying tray) of a drum-type washing machine or a fully automatic washing machine, in which a granular detergent composition allowed to stand in an aggregated state is distributed (flowed-in) into a washtub by pouring water,  
20 there often arise troubles that the granular detergent composition remains in the state of an aggregate (paste). Numerous studies for improving the distributivity of the granular detergent composition from the dispenser have been so far made. For instance, Japanese Unexamined Patent Publication No. Hei 7-509267 discloses a detergent composition comprising a base powder comprising particles  
25 including a particle having a size of less than 150  $\mu\text{m}$  in an amount of less than

10% by weight, and a particle having a size of greater than 1700  $\mu\text{m}$  in an amount of less than 10% by weight, and a fine powder or coarse grain of sodium carbonate, sodium citrate or the like as a filler. This art intends to increase the bulk density and the distributivity from the dispenser by reducing a surfactant-containing fine powder, or after-adding a fine powder or coarse grain of rapidly dissoluble non-gelated particle. In addition, Japanese Patent Laid-Open No. Hei 11-35998 discloses a granular high-density detergent of which 50% mass-base size, the constitution of a mass-base frequency at a particle size of less than 125  $\mu\text{m}$ , a mass-base frequency at a particle size of 1410  $\mu\text{m}$  or less, and a mass-base frequency at a specified particle size are limited within specified ranges. This art is intended to improve both the dispersibility of the granular detergent composition and the particle dissolubility by controlling the particle size distribution, and it is shown to be suitable for use in a disperser. According to these techniques, the dispersibility from a dispenser is improved, and the frequency of occurrence in the troubles that a pasty high-density detergent composition remains in the dispenser, or the amount remaining is reduced. However, there is yet a concern that the granular detergent composition may remain in the disperser depending upon a decrease of water pressure upon pouring water, a decrease in the water temperature, the means of water pouring, the form of the dispenser, or the like. Therefore, a further improvement in the distributivity of the granular detergent composition in the dispenser has been desired.

#### DISCLOSURE OF INVENTION

An object of the present invention is to provide a granular detergent

composition having excellent distributivity upon pouring water into a dispenser such as drum-type washing machines and fully automatic washing machines, composite detergent particles contained in the granular detergent composition, and detergent additive particles contained in the composite detergent particles.

5           These objects and other objects of the present invention will be apparent from the following description.

Specifically, the present invention relates to:

[1]   composite detergent particles prepared by dry-blending:

detergent additive particles (a) comprising 30 to 100% by weight of two  
 10 or more kinds of water-soluble substances, and further optionally comprising less than 10% by weight of a surfactant and/or 70% by weight or less of a water-insoluble substance, the detergent additive particles having an average particle size of from 150 to 600  $\mu\text{m}$ , a bulk density of 300 to 1000 g/L, and wherein the detergent additive particles have a dissolution rate of 90% or more, under  
 15 conditions where the detergent additive particles are supplied in water at 5°C; stirred for 60 seconds under the stirring conditions that 1 g of the detergent additive particles are supplied to a 1-L beaker (inner diameter: 105 mm) which is charged with 1-L of hard water (71.2 mg  $\text{CaCO}_3/\text{L}$ , a molar ratio of Ca/Mg: 7/3), and stirred with a stirring bar (length: 35 mm, and diameter: 8 mm) at a  
 20 rotational speed of 800 rpm; and filtered with a standard sieve having a sieve-opening of 74  $\mu\text{m}$  as defined by JIS Z 8801, wherein the dissolution rate of the detergent additive particles is calculated by Equation (1):

$$\text{Dissolution Rate (\%)} = \{1 - (T/S)\} \times 100 \quad (1)$$

wherein S is a weight (g) of the detergent additive particles supplied; and

25   T is a dry weight of insoluble remnants of the detergent additive particles

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remaining on the sieve when an aqueous solution prepared under the above stirring conditions is filtered with the sieve; and

detergent particles (b) having an average particle size of from 150 to 600  $\mu\text{m}$  and a bulk density of 500 to 1000 g/L, and comprising 10 to 50% by weight of a surfactant;

[2] a granular detergent composition comprising 50 to 100% by weight of the composite detergent particles of item [1]; and

[3] detergent additive particles (a) comprising 30 to 100% by weight of two or more kinds of water-soluble substances, and further optionally comprising less than 10% by weight of a surfactant and/or 70% by weight or less of a water-insoluble substance, the detergent additive particles having an average particle size of from 150 to 600  $\mu\text{m}$ , a bulk density of 300 to 1000 g/L, and wherein the detergent additive particles have a dissolution rate of 90% or more, under conditions where the detergent additive particles are supplied in water at 5°C; stirred for 60 seconds under the stirring conditions, and filtered with a standard sieve having a sieve opening of 74  $\mu\text{m}$  as defined by JIS Z 8801, wherein the dissolution rate of the detergent additive particles is calculated by Equation (1) mentioned above.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic view of a detergent additive particle observed from the surface centering about a cave-in hole, wherein S1 is a projected area which is measured centering about the opening of the cave-in hole, and S2 is a projected area of the hole measured as an opening.

Figure 2 is a schematic view of a cross section obtained by perpendicularly splitting the cave-in particle against the face centering about a cave-in hole as shown by a broken line in Figure 1 observed from a side face, wherein X is a tangent line of an open face of the cave-in hole; Y is a tangent line with the bottom of the hole in parallel to the tangent line X; and d is a distance between the tangent line X and the tangent line Y.

#### BEST MODE FOR CARRYING OUT THE INVENTION

In the present invention, it has been found that the distributivity in the dispenser of the composite detergent particles (a)+(b), obtainable by preparing detergent additive particles (a) having a specified composition containing no surfactant or having a little surfactant content, specified powder properties and a specified high dissolution rate, and mixing the detergent additive particles with detergent particles (b) containing a larger amount of a surfactant, is remarkably improved. Therefore, the troubles caused by the granular detergent composition remaining in the dispenser can be by far improved because the composite detergent particles are present in the granular detergent composition in a specified amount or higher.

The terminologies as used in the present invention will be described below.

##### 1. Definitions of Terminologies

The term "detergent additive particle" refers to a particle which can contain a surfactant in an amount of less than 10% by weight and a builder or the like, and the term "detergent additive particles" refers to an aggregate thereof.

Also, the term "detergent particle" refers to a particle comprising a surfactant in an amount of 10 to 50% by weight, and the term "detergent particles" refers to an aggregate thereof. In addition, the term "composite detergent particles" refers to an aggregate prepared by dry-blending the detergent additive particles and the detergent particles. The term "granular detergent composition" refers to a completed product of a granular detergent comprising the composite detergent particles prepared by dry-blending the detergent additive particles and the detergent particles, which encompasses those comprising particles comprising separately added detergent components (for instance, builder particles, fluorescent dyes, enzymes, perfumes, defoaming agents, bleaching agents, bleaching activators, and the like) as desired, other than the above-mentioned detergent additive particles and detergent particles.

## 2. Detergent Additive Particles (a)

The detergent additive particles of the present invention which exhibit excellent dispenser distributivity of the granular detergent composition by formulating the detergent additive particles as a component of the granular detergent composition contain no surfactant or have a very low surfactant content of less than 10% by weight. The detergent additive particles have the following characteristics.

### 2-1. Fast Dissolubility of Detergent Additive Particles

As a process of increasing the distributivity of the granular detergent composition by making discontinuous a continuous paste layer comprising a high-concentration surfactant, the paste layer being formed by the granular

detergent composition upon pouring water in the dispenser, the present invention is characterized in that detergent additive particles having a specified composition and specified powder properties are mixed with a granular detergent composition, and further that the detergent additive particles have the fast dissolubility described below.

Specifically, because of the fast dissolubility owned by the detergent additive particles mixed with the granular detergent composition, the formed paste layer comprising a high-concentration surfactant is rapidly made discontinuous upon pouring water, and at the same time there is an action of dissolving the detergent additive particles in the poured water at a fast rate, whereby the granular detergent composition can be rapidly and efficiently distributed from the dispenser. Here, when particles having a low dissolution rate are mixed with the detergent particles, the formed paste is rather hardened in the dispenser upon pouring water, so that the reduction in the distributivity from the dispenser is observed. Therefore, it is extremely important that the detergent additive particles have fast dissolubility.

The fast dissolubility owned by the detergent additive particles can be confirmed by showing a remarkably high dissolution rate in a case where individual constituent particles are dispersed in water. The fast dissolubility owned by the detergent additive particles of the present invention is such that a dissolution rate as calculated by the equation (1) is 90% or more in a case where the detergent additive particles are stirred for 60 seconds in accordance with the method described below, and filtered with a standard sieve having a sieve-opening of 74  $\mu\text{m}$  as defined by JIS Z 8801. In addition, the dissolution rate is preferably 92% or more, more preferably 94% or more, still more preferably

96% or more, still more preferably 97% or more, still more preferably 98% or more, most preferably 99% or more, from the viewpoint of further increasing the distributivity from the dispenser.

The method for confirming the fast dissolubility is detailed as follows.

5 A 1-L beaker (a cylindrical form having an inner diameter of 105 mm and a height of 150 mm, for instance, a 1-L glass beaker manufactured by Iwaki Glass Co., Ltd.) is charged with 1 L of hard water cooled to 5°C and having a water hardness corresponding to 71.2 mg CaCO<sub>3</sub>/L (a molar ratio of Ca/Mg: 7/3). With keeping the water temperature constant at 5°C with a water bath, water is  
10 stirred with a stirring bar [35 mm in length and 8 mm in diameter, for instance, commercially available from ADVANTEC, Model "TEFLON SA" (MARUGATA-HOSOGATA)] at a rotational speed (800 rpm), such that a depth of swirling to the water depth is about 1/3. The detergent additive particles which are sample-reduced and accurately weighed so as to be  $1.0000 \pm 0.0010$  g  
15 are supplied and dispersed in water with stirring, and stirring is continued. After 60 seconds from supplying the particles, a liquid dispersion of the particles in the beaker is filtered with a standard sieve (100 mm in diameter) and a sieve-opening of 74 μm as defined by JIS Z 8801 of a known weight. Thereafter, water-containing particles remaining on the sieve are collected in an open vessel  
20 of a known weight together with the sieve. Incidentally, the operation time from the start of filtration to collection with the sieve is set at 10 sec ± 2 sec. The insoluble remnants of the collected particles are dried for one hour in an electric dryer heated to 105°C. Thereafter, the dried insolubles are cooled by keeping in a desiccator with a silica gel at 25°C for 30 minutes. After cooling the insoluble  
25 remnants, a total weight of the dried insoluble remnants of the particles, the sieve

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and the collected vessel is measured, and the dissolution rate (%) of the detergent additive particles is calculated by the following Equation (1).

$$\text{Dissolution Rate (\%)} = \{1 - (T/S)\} \times 100 \quad (1)$$

wherein S is a weight (g) of the detergent additive particles supplied; and

T is a dry weight (g) of insoluble remnants of the detergent additive particles remaining on the sieve when an aqueous solution prepared under the above stirring conditions is filtered with the sieve.

A means for exhibiting a fast dissolubility of the detergent additive particles will be described in detail below.

#### 2-1-1. Fast Dissolubility by Particle Size Distribution Control

As one means for exhibiting a fast dissolubility when the detergent additive particles are dispersed in water, the adjustment of the particle size distribution of the detergent additive particles in consideration of the relationship between the size of the particles constituting the detergent additive particles and the dissolution rate is an effective means. In other words, for instance, a dissolution rate per unit time period is determined for the detergent additive particles which are classified in a plural steps by the sizes of the particle size. In a case where the dependability of the particle size on the dissolution rate is large, the fast dissolubility can be exhibited by reconstituting the particles so as to have a particle size distribution having a high dissolution rate by using the detergent additive particles which are classified with sieves.

#### 2-1-2. Fast Dissolubility by Void in Particle

As another means of exhibiting a fast dissolubility, the fast dissolubility

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can be attained by further increasing the dissolution rate of the particle constituting the detergent additive particles (detergent additive particle). The fast dissolubility can be exhibited by constructing the detergent additive particles with a particle having a fine void in the inner portion of the particle. In the detergent additive particle having a fine void in the inner portion, not only the detergent additive particle gradually dissolves from the surface but also water is allowed to enter into the fine void in the inner portion of the particle after the surface is dissolved, so that the particle is dissolved from the inner portion and the particle is disintegrated by the entered water, whereby the dissolution rate per unit time period can be increased. The fine void of the inner portion of the particle can be determined as a microporous capacity at 0.01 to 4  $\mu\text{m}$  by mercury porosimetry. It is preferable that the microporous capacity is 0.2 mL/g or more. In addition, the microporous capacity is more preferably a larger amount of 0.25 mL/g or more, still more preferably 0.3 mL/g or more, most preferably 0.35 mL/g or more; from the viewpoint of exhibiting an even more excellent fast dissolubility by allowing a greater amount of water to enter in the inner portion of the particle. Also, the microporous capacity is preferably 1.2 mL/g or less, more preferably 1.0 mL/g or less, still more preferably 0.8 mL/g or less, from the viewpoints of securing appropriate particle density and particle strength. When the microporous capacity of the detergent additive particles is determined, there can be employed a mercury porosimeter, for instance, one manufactured by SHIMADZU CORPORATION, "SHIMADZU Poresizer 9320." The microporous capacity is a value obtained for a microporous capacity at 0.01 to 4  $\mu\text{m}$  as determined for a sample-reduced detergent by a mercury porosimeter.

### 2-1-3. Fast Dissolubility by Releasing Bubble

As another means for exhibiting a fast dissolubility, the fast dissolubility can be exhibited by constructing the detergent additive particles with a detergent additive particle capable of releasing a bubble of 1/10 or more of the particle size in a process in which the detergent additive particle is dissolved in water (hereinafter referred to as "bubble-releasing detergent additive particle"). In the detergent additive particle, not only the dissolution takes place from the surface, but also water is allowed to enter into the inner portion of the particle along with the release of the bubble from the inner portion of the particle, so that the dissolution from the inner portion and the disintegration of the particle are caused by the entered water, whereby the dissolution ratio per unit time is increased.

The dissolution behavior described above can be confirmed by a digital microscope or optical microscope as a phenomenon in which a bubble of 1/10 or more, preferably 1/5 or more, more preferably 1/4 or more, still more preferably 1/3 or more, especially preferably 1/2 or more of the particle size of the particle (hereinafter referred to as "bubble having a given size") is released in the case where the bubble-releasing detergent additive particle is dissolved in water. Incidentally, in the case where the bubble-releasing detergent additive particle is dissolved in water with a stand-still state, the bubble having a given size is generated preferably within 120 seconds, more preferably within 60 seconds, still more preferably within 45 seconds, still more preferably within 30 seconds, still more preferably within 20 seconds, most preferably within 10 seconds.

The bubble-releasing detergent additive particle may have a single or a plurality of pores capable of releasing a bubble having a given size, and the

bubble-releasing detergent particle is not particularly limited in the form and structure of the particle. For example, the bubble-releasing detergent additive particle may be a detergent additive particle capable of releasing a single bubble, or it may be a detergent additive particle capable of releasing a plural bubbles in which the detergent additive particles are aggregated. In addition, the bubble-releasing detergent additive particle constitutes preferably 50% by weight or more, more preferably 60% by weight or more, still more preferably 70% by weight or more, still more preferably 80% by weight or more, most preferably 90% by weight or more, of the detergent additive particles.

When the detergent additive particles comprising a bubble-releasing detergent additive particle are mixed with the granular detergent composition, the distributivity can be improved also by the effect of the release of bubbles from the granular detergent composition upon pouring water in the dispenser and the effect of water entry caused by the release, in addition to the effect by the fast dissolubility.

The size of the bubble is measured as follows.

A double-sided adhesive tape is attached to a bottom center of a glass petri dish (inner diameter: 50 mm). The detergent additive particles are adhered to the double-sided adhesive tape. First, a projected area diameter ( $\alpha$   $\mu$ m) for each of the particles is determined from an image obtained by a digital microscope. As a digital microscope, for example, "VH-6300" manufactured by KEYENCE CORPORATION can be used.

Subsequently, 5 mL of ion-exchanged water at 20°C is poured into the glass petri dish, and the dissolution behavior for the individual particles of the subject measurement is observed. When the bubble is released from the inner

portion of the particle, the projected area diameter ( $\beta \mu\text{m}$ ) of the bubble is measured from an image of an instant at which the bubble leaves from the particle. Incidentally, in the case where a plurality of bubbles are released from the inner portion of the particle, " $\beta \mu\text{m}$ " is referred to a maximum value of the projected area diameter measured for each of the bubbles. The ratio of the bubble diameter to the particle size ( $\beta/\alpha$ ) for each of the particles is calculated.

In a preferable bubble-releasing detergent additive particle, it is preferable that a pore having a size of  $1/10$  to  $4/5$ , preferably  $1/5$  to  $4/5$ , more preferably  $1/4$  to  $4/5$ , still more preferably  $1/3$  to  $4/5$ , especially preferably  $1/2$  to  $4/5$ , of the particle size is present in the inner portion of the particle.

The pore size can be determined as follows.

The selected detergent additive particle is split at a cross section so as to include the maximum particle size without disintegrating the particle with a surgical knife, or the like. The split cross section is observed by a scanning electron microscope (SEM). A projected area diameter (particle size) [ $\gamma \mu\text{m}$ ] of a split cross section of the split particle and in the case where the presence of a pore in the inner portion of the particle is confirmed, a projected area diameter of the pore (pore size) [ $\delta \mu\text{m}$ ] are measured. Incidentally, in the case where a plurality of pores are confirmed, the projected area diameter  $\delta \mu\text{m}$  is defined as the largest pore size among them. Thereafter, the ratio of the pore size to the particle size ( $\delta/\gamma$ ) is calculated.

In addition, the shape of the preferable bubble-releasing detergent additive particle includes a shape having a structure that there exists a hollow in the inner portion of the particle, and a particle surface is opened and communicated with the hollow in the inner portion (particle surface being caved-in). Since the

detergent additive particle having a cave-in hole (cave-in particle) rapidly releases bubbles from the inner portion of the particle, water is allowed to enter into the inner portion of the particle quickly, so that there are advantages that the dissolution from the inner portion and the disintegration of the particle by the entered water are quickened.

In addition, the preferable size of the cave-in hole in the cave-in particle contained in the detergent additive particles of the present invention will be described. The projected area diameter of the particle can be obtained by photographing a particle using a microscope centering about the opening of the cave-in hole as shown in Figure 1, and calculating the projected area diameter from the equation (2) by using the projected area (S1) of the particle measured from the photographed particle image.

$$\begin{array}{l} \text{Projected Area Diameter} \\ \text{of Particle} \end{array} = 2 \times (S1/\pi)^{1/2} \quad (2)$$

In addition, the projected area diameter of the hole (cave-in hole) can be obtained by the equation (3) by using the projected area (S2) of the hole determined in the same manner as the projected area of the particle mentioned above with an opening.

$$\begin{array}{l} \text{Projected Area Diameter} \\ \text{of Hole} \end{array} = 2 \times (S2/\pi)^{1/2} \quad (3)$$

Here, as the microscope for the above measurement, there can be used, for instance, a digital microscope "VH-6300" manufactured by KEYENCE CORPORATION and SEM such as a field emission scanning electron

microscope "Model S-4000," manufactured by Hitachi, Ltd. In the calculation of the projected area, there can be used, for instance, WinRoof manufactured by Mitsutani, and the like.

A preferable diameter for the hole which is present in the cave-in particle contained in the detergent additive particles of the present invention is a hole in which:

$$\frac{(\text{Projected Area Diameter of Hole})}{(\text{Projected Area Diameter of Particle})} \times 100$$

is 2% or more. In addition, from the viewpoints that water is easily allowed to entered through the cave-in hole, and that a particle shape even closer to a spherical shape is desired for external appearance, the above ratio is more preferably from 2 to 70%, still more preferably from 4 to 60%, still more preferably from 6 to 50%, still more preferably from 8 to 40%, most preferably from 10 to 30%.

The depth of the hole which is present in the particle contained in the detergent additive particles of the present invention is expressed by the ratio of a distance *d* between a tangent line X of an open surface of the cave-in hole and a tangent line Y with the bottom of the hole in parallel to the tangent line X as shown in Figure 2 to the projected area diameter of the particle described above, i.e.,

$$\frac{(\text{Distance } d)}{(\text{Projected Area Diameter of Particle})} \times 100$$

Here, the depth of the hole can be determined, for instance, by splitting a particle with a surgical knife or the like at a plane perpendicular to the open hole portion

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of the cave-in hole as shown by the broken line in Figure 1, and photographing the cross section with SEM or the like. It is preferable that the depth of the hole which is present in the cave-in particle contained in the detergent additive particles of the present invention is such that the ratio as defined above is 10% or more. In addition, from the viewpoints of even more increasing the amount of water entered into the inner portion of the particle and even more securing the strength of the particle, the ratio is more preferably from 10 to 90%, still more preferably from 15 to 80%, especially preferably from 20 to 70%.

It is preferable that the cave-in particle is contained in an amount of 50% by weight or more, more preferably 60% by weight or more, still more preferably 70% by weight or more, still more preferably 80% by weight or more, most preferably 90% by weight or more, of the detergent additive particles.

#### 2-1-4. Fast Dissolubility by Localized Structure of Composition

Apart from, or together with the bubble-releasing mechanism described above for remarkably enhancing the dissolution rate of the detergent additive particle, a fast dissolubility can be exhibited from the surface of the particle. The characteristic thereof is such that the particle constituting the particles which is obtained by the drying step and used for the detergent additive particles or for principal constituents of the detergent additive particles has a localized structure in which the composition near the surface of the particle is different from that of the inner portion thereof. For instance, in a case where the particle obtained by the drying step comprises a water-soluble substance and a water-insoluble substance, by having a localized structure in which the water-soluble substance is present in a larger amount near the surface of the particle than in the inner



portion thereof, the water-soluble substance near the surface more quickly dissolves in water, so that there is exhibited a dissolution behavior of accelerating the disintegration from the surface of the particle, whereby a fast dissolubility can be exhibited. Here, the term "water-soluble substance" refers to a compound of which solubility is 0.5 g / 100 g or more to water at 25°C, among which the term "water-soluble salt" refers to those having a molecular weight of less than 1000, and the term "water-soluble polymer" refers to an organic polymer having a molecular weight is 1000 or more. The term "water-insoluble substance" refers to those of which solubility is less than 0.5 g / 100 g of water at 25°C. In addition, even when the particle obtained by the drying step is only composed of the water-soluble substance, a fast dissolubility can be exhibited by having a localized structure in which the composition near the surface of the particle is different from that in the inner portion thereof. For instance, in the case where the particle comprises a water-soluble polymer and a water-soluble salt, since the particle has a localized structure in which the water-soluble polymer is present in a larger amount near the surface of the particle than that in the inner portion thereof, there can be exhibited a fast dissolubility by showing a dissolution behavior that the water-soluble polymer near the surface more quickly dissolves in water and that the strength of the particle is lowered, thereby accelerating the disintegration of the particle. Here, the most preferable embodiment for exhibiting a fast dissolubility is detergent additive particles which have a localized structure of the composition, and fine voids, more preferably a hollow, in the inner portion of the particle, a particle surface being opened and communicated with the hollow in the inner portion.

The localized structure is confirmed as follows.

As a method for confirming the localized structure, there can be employed, for instance, a combined method of Fourier transform infrared spectroscopy (FT-IR) and photoacoustic spectroscopy (PAS) (simply abbreviated as "FT-IR/PAS"). As described in "*APPLIED SPECTROSCOPY*," 47, 1311-1316 (1993), the distribution state of the substances in the direction of depth from the surface of the samples can be confirmed by the method.

The measurement method for determining the structure of the detergent additive particle of the present invention will be exemplified below.

Each cell is charged with the detergent additive particles of two different states to conduct FT-IR/PAS measurement, and the structure of the detergent additive particle can be determined by comparing the measurement values. In other words, one FT-IR/PAS measurement is taken for the detergent additive particles in a state where the desired structure is retained, and another FT-IR/PAS measurement is taken for the comparative sample in which the detergent additive particles are in a uniform state by sufficiently grinding the detergent additive particles with an agate mortar or the like. The FT-IR/PAS is measured, for instance, by using an infrared spectrometer "FTS-60A/896" (manufactured by Bio-Rad Laboratories), and a photoacoustic detector "Model 300" as the PAS cell (manufactured by MTEC Corporation). The measurement conditions are resolution of  $8\text{ cm}^{-1}$ , scanning speed of  $0.63\text{ cm/s}$ , and 128 scans. In the above measurement conditions, the information up to a depth of about  $10\text{ }\mu\text{m}$  from the particle surface of the detergent additive particles is included. In the PAS spectra of the detergent additive particles, each of the characteristic peaks of sodium carbonate, sodium sulfate, zeolite and sodium polyacrylate can be read off at  $1434\text{ cm}^{-1}$  ( $\text{CO}_3^{2-}$  degenerate stretching vibration),  $1149\text{ cm}^{-1}$  ( $\text{SO}_4^{2-}$  degenerate

stretching vibration),  $1009\text{ cm}^{-1}$  (Si-O-Si anti-symmetric stretching vibration), and  $1576\text{ cm}^{-1}$  ( $\text{CO}_2^-$  anti-symmetric stretching vibration), respectively, and the areal intensity of each peak is measured. The relative areal intensity of each of the characteristic peaks of the water-soluble salt such as sodium carbonate or sodium sulfate to the characteristic peaks of one substance, for instance, the zeolite, when measured for each of the state in which the structure of the detergent additive particle is retained, and the state in which the detergent additive particle is uniformly ground, is obtained. The resulting relative intensity is then compared with the relative areal intensity of the characteristic peaks of the water-soluble polymer to the characteristic peaks of the zeolite, when measured for each of the above states, and thereby the structural features of the detergent additive particles can be determined. As the above example is concretely explained, it can be proven that the detergent additive particle has a localized structure such that a larger amount of the water-soluble polymer and/or the water-soluble salts is included near the surface of the particle than the inner portion thereof, and that a larger amount of the water-insoluble substance is included in the inner portion of the particle than near the surface thereof. Even in examples other than those described above where two or more substances which can be subjected to FT-IR/PAS are present, the localized structure can be proven by comparing the relative areal intensities of these characteristic peaks.

With respect to the detergent additive particles, ratios of the relative areal intensity based on the characteristic peaks of a given standard substance (a substance which is present in a larger amount in the inner portion of the particle than near the surface thereof being selected) when measured in the state in which the localized structure of the components is retained to the relative areal intensity

based on the characteristic peaks of the above-mentioned standard substance when measured in the state in which the detergent additive particle is ground to give a uniform state are calculated. In at least one substance of those other than the standard substance mentioned above, the ratio is 1.1 or more, and from the viewpoint of exhibiting a more excellent fast dissolubility, the ratio is preferably 1.2 or more, more preferably 1.3 or more, still more preferably 1.4 or more, especially preferably 1.5 or more. The detergent additive particle can be said to have a localized structure when the detergent additive particle has these ratios of relative areal intensities.

As other method of determination, there can be employed energy dispersion-type X-ray spectroscopy (EDS) and electron probe microanalysis (EPMA). By these analysis methods, two-dimensional distribution of elements can be analyzed by scanning the sample surface with an electron beam.

For instance, as the energy dispersion-type X-ray diffractometer, there can be employed "EMAX 3770" manufactured by Horiba, LTD. which is attached to SEM such as a field emission scanning electron microscope "Model S-4000," manufactured by Hitachi, Ltd. For instance, in the case where the water-soluble salts, the water-insoluble substance, and the water-soluble polymer are contained in the detergent additive particle, the distribution state of elements measured with respect to C, Na, Al, Si, S, and the like of the split cross section of the detergent additive particle obtained by embedding the detergent additive particle with a resin and splitting the embedded particle with a microtome, is such that C, Na and S are present in large amounts in the outer side of the particle cross section, and that Al and Si are present in large amounts in the central portion. Therefore, there can be confirmed the structure in which large amounts of the water-soluble

salts are included near the surface of the detergent additive particle, and a large amount of the water-insoluble substance is included in the central portion.

## 2-2. Composition of Detergent Additive Particles (a)

5           The detergent additive particles of the present invention are those comprising 30 to 100% by weight of two or more kinds of water-soluble substances, and further optionally comprising less than 10% by weight of a surfactant and/or 70% by weight or less of a water-insoluble substance. The term "water-soluble substance" in the present invention refers to a compound of which solubility is 0.1 g or more to 100 g of purified water at 20°C, and the term "water-insoluble substance" refers to a compound of which dissolved amount is less than 0.1 g to 100 g of purified water at 20°C. However, the crystalline silicate in the present invention is treated as a water-insoluble substance, and the surfactant is treated so as not to include in both the water-soluble substance and the water-insoluble substance.

10           The compositional feature of the detergent additive particles of the present invention resides in that the particles contain no surfactant or only have a very little surfactant content. The content of the surfactant is less than 10% by weight. By mixing the detergent additive particles with a granular detergent composition having a larger formulation amount of the surfactant, there is exhibited an effect of making discontinuous a paste layer comprising a surfactant formed by the granular detergent composition upon pouring water into the dispenser, whereby the distributivity of the dispenser can be increased. In addition, the preferred content of the surfactant mentioned above is from 0 to 8% by weight, more preferably less than 6% by weight, still more preferably less than 4% by weight,

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still more preferably less than 2% by weight, still more preferably less than 1% by weight, most preferably containing substantially no surfactant, from the viewpoint of exhibiting a more excellent effect.

In order to exhibit an effect of making discontinuous a paste layer comprising a surfactant formed by the granular detergent composition upon pouring water into the dispenser as well as to exhibit the fast dissolubility in the detergent additive particles, it is required that the water-soluble substance in the present invention is formulated in an amount of 30 to 100% by weight. In addition, the content of the water-insoluble substance is preferably 40% by weight or more, more preferably 50% by weight or more, still more preferably 60% by weight or more, still more preferably 70% by weight or more, still more preferably 80% by weight or more, still more preferably 90% by weight or more, most preferably essentially consisting of only the water-soluble substance, from the viewpoints of enhancing the above-mentioned effects by reducing the surfactant content mentioned above and the content of the water-insoluble substance mentioned below.

In order to improve the distributivity from a dispenser by alleviating the phenomenon of curing the formed paste comprising the granular detergent composition when water is poured in the dispenser, namely the phenomenon of a lowered flowability of the water-containing granular detergent composition due to the rheology properties exhibited when the water-insoluble substance is mixed with water, it is required that the content of the water-insoluble substance in the present invention is 70% by weight or less. In addition, the content of the water-insoluble substance is preferably 60% by weight or less, more preferably 50% by weight or less, still more preferably 40% by weight or less, still more preferably

30% by weight or less, still more preferably 20% by weight or less, still more preferably 10% by weight or less, most preferably essentially containing no water-insoluble substance, from the viewpoints of suppressing the curing of the granular detergent composition by the water-insoluble substance described above, thereby further increasing the distributivity from the dispenser.

#### 2-2-1. Water-Soluble Substance

The water-soluble substance in the present invention includes, for instance, water-soluble inorganic salts such as alkali metal salts, ammonium salts, amine salts, and the like, each having a carbonate group, a hydrogencarbonate group, a sulfate group, a sulfite group, a hydrogensulfate group, a chloride group, a bromate group, an iodate group, a silicate group, a phosphate group, and the like; and water-soluble organic salts having a low molecular weight such as citrates and fumarates (provided that a surfactant is not included herein). Among them, the carbonate group, the sulfate group and the sulfite group are preferable. The water-soluble inorganic salt is preferable because the disintegration of the detergent additive particles in water can be accelerated by generating heat of hydration and heat of dissolution by the reaction with water, and the self-disintegration of the particle can be accelerated by expanding the bubbles in a case where the detergent additive particle is a bubble-releasing particle.

It is preferable that the water-soluble substance is contained in plural kinds than a single kind. When the water-soluble substance is a single kind of the water-soluble substance, for instance, sodium carbonate, sodium sulfate, or the like, for forming a hydration crystal at a low temperature, if the temperature of the poured water is high, the distributivity of the granular detergent

composition is sufficiently improved by an effect of making discontinuous a paste layer comprising a high-concentration surfactant by mixing with the detergent additive particles. However, if water having a lower temperature is poured, the water-soluble substance is precipitated as a hydrated crystal, so that there arises a phenomenon that the water-containing granular detergent composition is cured, whereby the effect of improving the distributivity of the dispenser by mixing the detergent additive particles tends to be lowered. From the viewpoint of exhibiting an excellent effect of improving the distributivity of the detergent additive particles even when water is poured at a low temperature, a preferable mode of containing the water-soluble substance is a case where a water-soluble substance for forming a hydration crystal in water at a low temperature, and a water-soluble substance for precipitating the crystal by lowering the solubility by a decrease in the water temperature, and the like are contained. By the copresence of two or more kinds of the water-soluble substances, the growth of the hydration crystals by a single water-soluble substance can be preferably suppressed or delayed. More specifically, on the basis of one kind of the water-soluble substance contained in the detergent additive particles, other one or more kinds of the water-soluble substances are contained in a molar ratio of preferably 9/1 or less, more preferably 8/2 or less, still more preferably 7/3 or less, especially preferably 6/4 or less, most preferably approximate 5/5.

In addition, sodium carbonate is also preferable as an alkalizing agent for showing a suitable pH buffering region in a washing liquid. The alkalizing agents other than those mentioned above include amorphous silicates. In addition, salts having a high degree of dissociation such as sodium sulfate,



potassium sulfate, and sodium sulfite enhance an ionic strength of a washing liquid, and favorably act to detergency against sebum stains. In addition, a sulfite group reduces hypochlorite ions contained in tap water, and has an effect of preventing detergent components such as enzymes and perfumes from oxidation degradation. In addition, sodium tripolyphosphates, which have excellent metal ion capturing ability and the alkalizing ability, can also be suitably used. As the water-soluble organic acid salts having low-molecular weights, those base materials having a large  $pKCa^{2+}$  and/or having a large cationic exchange capacity are preferable in expectation of imparting the metal ion capturing ability. Besides the citrates, there can be also included methyliminodiacetates, iminodisuccinates, ethylenediaminedisuccinates, taurine diacetates, hydroxyethyliminodiacetates,  $\beta$ -alanine diacetates, hydroxyiminodisuccinates, methylglycine diacetates, glutamine diacetates, asparagine diacetates, serine diacetates, and the like.

Besides the above, there are included water-soluble polymers. The water-soluble polymer is preferable, from the viewpoint of having an effect of enhancing the particle strength of the detergent additive particle, when the detergent additive particles of the present invention are obtained by a process including a drying step, together with the viewpoint of having an action of giving a bubble-releasing structure in the particle, a localized structure of the compositions, a fine void in the inner portion of the particle, and further giving a shape having a structure that there exists a hollow in the inner portion of the particle, and a particle surface is opened and communicated with the hollow in the inner portion, in a case where the drying step is a spray-drying step. From the viewpoints of giving an appropriate strength to the detergent additive particle

and a particle structure which is capable of exhibiting fast dissolubility in the spray drying, it is preferable that the water-soluble polymer is contained in an amount of from 1 to 40% by weight, more preferably from 2 to 30% by weight, still more preferably from 3 to 20% by weight, still more preferably from 4 to 15% by weight, especially preferably from 5 to 10% by weight, of the detergent additive particles. The water-soluble polymer includes, for instance, carboxylic acid-based polymers; carboxymethyl celluloses; water-soluble starches; sugars; and the like. Among them, the carboxylic acid-based polymers are preferable, from the viewpoint of enhancing the detergency of the granular detergent composition. Among these, salts of acrylic acid-maleic acid copolymers, and polyacrylates (Na, K,  $\text{NH}_4$ , and the like) are especially excellent.

The molecular weight of the water-soluble polymers is from 1000 to 100000, more preferably from 2000 to 80000, especially preferably from 5000 to 50000.

Besides the carboxylic acid-based polymers mentioned above, polymers such as polyglyoxylates; cellulose derivatives such as carboxymethyl celluloses; and aminocarboxylic acid-based polymers such as polyaspartates have an ability of capturing metal ions, a dispersibility, and an ability of preventing re-deposition.

Other polymers include polyvinyl pyrrolidones (PVP), polyethylene glycols (PEG), polypropylene glycols (PPG), and the like. The PVA is preferable as a dye-transfer inhibitor, and the PEG and the PPG having a molecular weight of from about 100 to about 20000 are preferable, because the viscosity of a paste, which is formed by containing water of aggregates of the granular detergent composition of the present invention, is improved.

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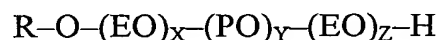
### 2-2-2. Surfactant

As the surfactant in the present invention, there can be used one or more kinds selected from the group consisting of anionic surfactants, nonionic surfactants, cationic surfactants and amphoteric surfactants. The anionic surfactants are exemplified by alkylbenzenesulfonates; alkyl ether or alkenyl ether sulfates;  $\alpha$ -olefinsulfonates; salts of  $\alpha$ -sulfonated fatty acids or esters thereof; alkyl ether or alkenyl ether carboxylates, amino acid-type surfactants; N-acyl amino acid-type surfactants, and the like. Especially included are linear alkylbenzenesulfonates of which alkyl moiety has 10 to 14 carbon atoms; and alkyl sulfates or alkyl ether sulfates, of which each alkyl moiety has 10 to 18 carbon atoms. The counter ions are preferably sodium, potassium, monoethanolamine, diethanolamine, and the like.

Further, in order to obtain defoaming effects, a salt of a fatty acid having 12 to 18 carbon atoms can be used in combination therewith.

The nonionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene-polyoxypropylene alkyl ethers, polyoxyethylene-polyoxypropylene glycols as represented by the trade name "pluronic," polyoxyethylene alkylamines, higher fatty acid alkanolamides, alkyl glucosides, alkyl glucosamides, alkylamine oxides, and the like. Among them, those having high hydrophilicity and/or those having a low forming ability of liquid crystals or having no formation of liquid crystals when mixed with water are preferable, and the polyoxyalkylene alkyl ethers are especially preferable. Preferable are ethylene oxide (hereinafter referred to as EO) adducts of which alcohol moiety has 10 to 18 carbon atoms, preferably 12 to 14 carbon

atoms, and an average mole of ethylene oxide of 5 to 30 moles, preferably 7 to 30 moles, more preferably 9 to 30 moles, especially preferably 11 to 30 moles; the EO adducts and propylene oxide (hereinafter referred to as PO) adducts, each of which alcohol moiety has 8 to 18 carbon atoms. As the order of addition, there can be employed embodiments including an embodiment of adding EO, and thereafter adding PO; an embodiment of adding PO, and thereafter adding EO; or an embodiment of adding randomly EO and PO. Especially preferable order of addition includes an embodiment of adding EO, thereafter adding PO in a block form, and further adding EO in a block form to give a compound represented by the general formula:



wherein R is an alkyl group or an alkenyl group; EO is an oxyethylene group; PO is an oxypropylene group; and X, Y and Z are each average moles thereof, among which most preferable average moles have the relations of  $X > 0$ ;  $Z > 0$ ;  $X+Y+Z = 6$  to  $14$ ;  $X+Z = 5$  to  $12$ ; and  $Y = 1$  to  $4$ .

The cationic surfactants include quaternary ammonium salts such as alkyl trimethyl ammonium salts.

The amphoteric surfactants are exemplified by carbobetain-type and sulfobetain-type surfactants and the like.

### 2-2-3. Water-Insoluble Substance

The water-insoluble inorganic substance, which is a water-insoluble substance is preferably those which are fine having a primary particle size of from  $0.1 \mu m$  to less than  $20 \mu m$ , from the viewpoint of quality. The water-

insoluble inorganic substance includes, for instance, crystalline or amorphous aluminosilicates, silicon dioxide, hydrated silicate compounds, clay compounds such as perlite and bentonite, and the like, among which crystalline or amorphous aluminosilicates, silicon dioxide and hydrated silicate compounds are favorably used. In particular, the crystalline aluminosilicates are preferable as a metal ion capturing agent.

The (average) primary particle size of the crystalline aluminosilicate may be 0.1  $\mu\text{m}$  to less than 20  $\mu\text{m}$ . In considerations of the cationic exchange speed and the residuality onto laundered clothes, the smaller the primary particle size the better. The particle size can be confirmed by a scanning electron microscope. In addition, aggregates of the primary particles can be used. For instance, A-type zeolites can be used, from the viewpoints of the metal ion capturing ability and the costs. In addition, when a support of a liquid component, for instance, a liquid surfactant, by the detergent additive particles is required, a use of a water-insoluble substance having an oil-absorbing ability is effective. The value of the oil-absorbing ability of A-type zeolite determined by the method according to JIS K 5101 is preferably from 40 to 50 mL/100 g (for instance, trade name: "TOYOBUILDER," manufactured by Tosoh Corporation). Besides the above, there are included P-type (for instance, trade names: "Doucil A24," "ZSE064" and the like; manufactured by Crosfield B.V.; oil-absorbing ability: 60 to 150 mL/100 g); and X-type zeolite (for instance, trade name: "Wessalith XD"; manufactured by Degussa-AG; oil-absorbing ability: 80 to 100 mL/100 g). A hybrid zeolite described in WO 98/42622 can be also included as preferable crystalline aluminosilicates.

In addition, amorphous silicas, amorphous aluminosilicates, and the like,

which have a high oil-absorbing ability but a low metal ion capturing ability, can be used as the water-insoluble substances. Examples include amorphous aluminosilicates including those described in Japanese Patent Laid-Open No. Sho 62-191417, page 2, lower right column, line 19 to page 5, upper left column, line 17 (especially, the initial temperature being preferably within the range from 15° to 60°C); and those described in Japanese Patent Laid-Open No. Sho 62-191419, page 2, lower right column, line 20 to page 5, lower left column, line 11 (especially, the oil-absorbing amount being 170 mL/100 g); amorphous aluminosilicates (oil-absorbing ability: 285 mL/100 g) described in Japanese Patent Laid-Open No. Hei 9-132794, column 17, line 46 to column 18, line 38; Japanese Patent Laid-Open No. Hei 7-10526, column 3, line 3 to column 5, line 9; Japanese Patent Laid-Open No. Hei 6-227811, column 2, line 15 to column 5, line 2; Japanese Patent Laid-Open No. Hei 8-119622, column 2, line 18 to column 3, line 47, and the like. For instance, there can be used oil-absorbing carriers, for instance, "TOKSIL NR" (manufactured by Tokuyama Soda Co., Ltd.; oil-absorbing ability: 210 to 270 mL/100 g); "FLOWRITE" (the same as above; oil-absorbing ability: 400 to 600 mL/100 g); "TIXOLEX 25" (manufactured by Kofran Chemical; oil-absorbing ability: 220 to 270 mL/100 g); "SILOPURE" (manufactured by Fuji Devison Co., Ltd.; oil-absorbing ability: 240 to 280 mL/100 g), and the like. Especially, as the oil-absorbing carriers, favorable are those described in Japanese Patent Laid-Open No. Hei 6-179899, column 12, line 12 to column 13, line 1, and column 17, line 34 to column 19, line 17.

In addition, it is preferable to contain a crystalline silicate in the water-insoluble substance in the present invention. Those crystalline silicates

described in European Patent Publication 0630855, page 18 (preferably the crystalline silicate obtained in Example 23); Japanese Patent Laid-Open No. Hei 5-279013, column 3, line 17 to column 6, line 24 (especially, those prepared by a process comprising calcinating and crystallizing at a temperature of from 500° to 1000°C being preferable); Japanese Patent Laid-Open No. Hei 7-89712, column 2, line 45 to column 9, line 34; and Japanese Patent Laid-Open No. Sho 60-227895, page 2, lower right column, line 18 to page 4, upper right column line 3 (especially the silicates in Table 2 being preferable) can be cited as base materials having both the alkalizing ability and the metal ion capturing agent. Here, the alkali metal silicates having an  $\text{SiO}_2/\text{M}_2\text{O}$  ratio, wherein M is an alkali metal, of preferably from 0.5 to 3.2, more preferably from 1.5 to 2.6, are favorably used. A preferable formulation process includes a process comprising finely pulverizing the crystalline silicate to a size of 1  $\mu\text{m}$  to less than 20  $\mu\text{m}$ , preferably to a size of 1  $\mu\text{m}$  to less than 10  $\mu\text{m}$ , and thereafter using the pulverized product as a surface-modifying agent.

### 2-3. Powder Properties of Detergent Additive Particles

Next, the powder properties of the detergent additive particles of the present invention will be explained.

#### 2-3-1. Average Particle Size

The average particle size of the detergent additive particles of the present invention is measured by vibrating a sample with each of standard sieves according to JIS Z 8801 for 5 minutes, and thereafter determining from a weight percentage depending upon the size openings of the sieves. The average particle

size of the detergent additive particles is adjusted to 150  $\mu\text{m}$  or more, in order to suppress the powdering when handling the granular detergent composition which is mixed with the particles, and the average particle size is adjusted to 600  $\mu\text{m}$  or less, in order to secure the fast dissolubility of the detergent additive particles. In order to satisfy both of the above requirements and also suppress the classification of the detergent additive particles in the granular detergent composition, the average particle size is preferably from 170 to 500  $\mu\text{m}$ , more preferably from 180 to 450  $\mu\text{m}$ , still more preferably from 190 to 400  $\mu\text{m}$ , most preferably from 200 to 350  $\mu\text{m}$ . In addition, from the viewpoints of suppressing the classification of the detergent additive particles in the granular detergent composition, thereby constantly exhibiting an effect of improving the dispersibility of a dispenser by the particles, and at the same time effectively making discontinuous by the particles, the formed paste layer comprising the surfactant, when water is poured to the granular detergent composition, it is preferable that the average particle size approximates the average particle size of the detergent particles (b) described below. The preferred difference in the average particle sizes between the detergent additive particles and the detergent particles (b) is preferably within 350  $\mu\text{m}$ , more preferably within 300  $\mu\text{m}$ , still more preferably within 250  $\mu\text{m}$ , still more preferably within 200  $\mu\text{m}$ , still more preferably within 150  $\mu\text{m}$ , still more preferably within 100  $\mu\text{m}$ , most preferably within 50  $\mu\text{m}$ .

#### 2-3-2. Bulk Density

The bulk density of the detergent additive particles of the present invention is measured by a method according to JIS K 3362. The bulk density is



from 300 to 1000 g/L, preferably from 320 to 900 g/L, more preferably from 340 to 850 g/L, still more preferably from 360 to 800 g/L, still more preferably from 380 to 750 g/L, still more preferably from 400 to 700 g/L, most preferably from 420 to 650 g/L, in order to impart a more excellent fast dissolubility, and to improve the dispersibility of the granular detergent composition which is mixed with the detergent additive particles in the dispenser, and also to provide a bulk density of the granular detergent composition in a preferable range and to suppress the classification of the detergent additive particles in the granular detergent composition.

#### 2-4. Process for Preparing Detergent Additive Particles

The detergent additive particles of the present invention are prepared by a process comprising the following steps (X) and (Y):

Step (X): preparing a solution or suspension comprising a water-soluble substance, and further comprising a surfactant and/or a water-insoluble substance as occasion demands (hereinafter referred to as "slurry or the like").

Here, in the present invention, the term "solution" refers to an aqueous solution of a water-soluble substance, or an aqueous solution of a water-soluble substance and a surfactant, and the term "suspension" refers to those containing undissolved substances of the water-soluble substance and/or the water-insoluble substance, which encompass those in the forms of slurries and pastes.

Step (Y): drying a slurry or the like obtained in Step (X).

The detergent additive particles of the present invention are prepared by including the steps mentioned above. As occasion demands, a step of adjusting the particle size distribution described below can be added. As the step of

adjusting the particle size distribution, for instance, there can be added a step of disintegration and pulverization for obtaining a desired particle size, a classification step using sieves, a step of disintegration and pulverization of coarse grains generated in the classification step, a readjustment step of the particle size distribution using air or plural-step sieves, and the like. The addition of the readjustment step of the particle size distribution is especially preferable, from the viewpoint of imparting the fast dissolubility to the particles, when the particles obtained in Step (Y) do not have fast dissolubility owing to bubble-releasing ability, a localized structure of the composition, and fine voids in the inner portion of the particles, and further have a hollow in the inner portion of the particle, a particle surface being opened and communicated with the hollow in the inner portion.

In addition, there may be added as occasion demands a step of after-adding a surfactant or a precursor thereof within an amount limited to the compositional range of the detergent additive particles of the present invention; a step of after-adding a water-soluble substance in the form of a paste, a slurry, or a solution; or a step of after-adding a water-insoluble substance having a size of 1  $\mu\text{m}$  to less than 20  $\mu\text{m}$  and a water-soluble substance having a size of 1  $\mu\text{m}$  to less than 20  $\mu\text{m}$ , thereby depositing the after-added substances to the particle surface. However, a total amount of the after-added substances in the after-addition step, as expressed by a weight ratio based on the particles obtained in the drying step (Y), is preferably 1/4 or less, more preferably 1/9 or less, still more preferably 1/19 or less, still more preferably 1/49 or less, still more preferably 1/99 or less, most preferably no after-addition, in order to sufficiently exhibit the effect of improving the distributivity in the dispenser owned by the

particle obtained in the drying step (Y) mentioned above.

The preferable embodiments for Steps (X) and (Y) will be described below.

5      2-4-1.    Step (X)

The slurry or the like may be those which are liquid-conveyable with a pump, and non-curable. The addition method of the components and the order can be appropriately varied depending upon the conditions. In addition, the content of each component such as the water-soluble substance in the slurry or the like is as described above.

10      2-4-2.    Step (Y)

Regarding the drying process, any of drying processes, for instance, freeze-drying, drying under reduced pressure and the like, can be employed. In order that a structure of the particle after drying takes a structure having a void of a volume of 0.2 mL/g or more in the inner portion of the particle, a structure having a hole capable of releasing a bubble of a size of 1/10 or more of the particle size of the particle, a structure having a cave-in hole and/or a structure having the localizability of the components, it is preferable that the slurry or the like is instantly dried, and an especially preferable drying process is a spray-drying process.

20      3.        Detergent Particles (b)

As the detergent particles, the detergent particles which are usable for ordinary granular detergent compositions can be used. The detergent particles

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may be prepared by any process, so long as the detergent particles have the composition and powder properties described below.

The component supplementing the detergency by the surfactant which is deficient in the detergent additive particles (a) mentioned above is detergent particles (b) which contain 10% by weight or more of a surfactant. The detergent particles (b) are dry-blended with the detergent additive particles (a), to give composite detergent particles having excellent distributivity in the dispenser. In addition, when the surfactant contained in the detergent particles (b) is a surfactant having a crystal-forming ability, the distributivity improvement effects in the dispenser are more remarkably exhibited by dry-blending the detergent additive particles (a) with the detergent particles, to give composite detergent particles. Here, the term "surfactant having a crystal-forming ability" refers to a surfactant in which liquid crystals having a water content in the range of 0 to 99%, and being observed in the form of lamella, hexagonal or the like in a temperature range of 5° to 70°C.

### 3-1. Composition of Detergent Particles (b)

The content of the surfactant in the detergent particles (b) is from 10 to 50% by weight, preferably from 15 to 49% by weight, more preferably from 20 to 48% by weight, still more preferably from 25 to 47% by weight, especially preferably from 30 to 46% by weight, of the detergent particles (b), in order to impart detergency to the composite detergent particles and to give desired powder properties in the detergent particles.

The detergent particles comprise an anionic surfactant and/or a nonionic surfactant, and may comprise a cationic surfactant and an amphoteric surfactant

as occasion demands.

Here, as to these surfactants, the same ones as those which are exemplified in the detergent additive particles mentioned above can be exemplified.

5 In addition, the detergent particles can contain a water-soluble substance as a component other than the surfactant mentioned above. The preferred content of the water-soluble substance is from 20 to 90% by weight. As the water-soluble substance usable in the detergent particles, the same ones as those which are exemplified as the water-soluble substance in the detergent additive  
10 particles mentioned above can be exemplified.

The detergent particles can further comprise a water-insoluble substance as desired. The preferred content of the water-insoluble substance is from 0 to 70% by weight. As the water-insoluble substance usable in the detergent  
15 particles, the same ones as those which are exemplified in the detergent additive particles mentioned above can be exemplified.

### 3-2. Powder Properties of Detergent Particles (b)

#### 3-2-1. Average Particle Size

20 The average particle size of the detergent particles, as determined by using standard sieves according to JIS Z 8801, is adjusted to 150  $\mu\text{m}$  or more, in order to suppress the powdering when handling the granular detergent composition comprising the detergent particles, and the average particle size is adjusted to 600  $\mu\text{m}$  or less, in order to secure the dissolubility of the detergent  
25 particles in a washtub after being distributed from the dispenser. The average

particle size is more preferably from 170 to 500  $\mu\text{m}$ , still more preferably from 180 to 450  $\mu\text{m}$ , still more preferably from 190 to 400  $\mu\text{m}$ , most preferably from 200 to 350  $\mu\text{m}$ .

5 3-2-2. Bulk Density

The bulk density of the detergent particles, as measured by a method according to JIS K 3362, is from 500 to 1000 g/L. The bulk density is preferably from 550 to 1000 g/L, more preferably from 600 to 1000 g/L, still more preferably from 650 to 1000 g/L or more, especially preferably from 700 to 1000 g/L, in considerations of the improvement in the transportation efficiency of the granular detergent composition comprising the detergent particles, and the convenience of the users.

10 3-3. Process for Preparing Detergent Particles (b)

15 As the process for preparing detergent particles, there can be employed a process comprising obtaining a spray-dried particle from a surfactant and a builder, and increasing the bulk density of the resulting spray-dried particle, and the like. This process includes, for instance, a process of increasing the bulk density by granulating the spray-dried particles in a vertical or horizontal mixer with agitation. As such processes, there can be employed, for instance, a process comprising granulating a spray-dried particle with agitation as described in Japanese Patent Laid-Open No. Sho 61-69897; a process comprising molding a dried particle and disintegrating and granulating the dried particle as described in Japanese Patent Laid-Open No. Sho 62-169900; a process comprising  
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25 disintegrating a solid detergent obtained by mixing and blending raw detergent

materials as described in Japanese Patent Laid-Open No. Sho 62-236897; as a process without using a spray-drying tower from the viewpoint of conservation of energy, a process comprising neutralizing an acid precursor of an anionic surfactant with a granular solid alkalizing agent in a dry state in a high-speed mixer, and granulating the resulting neutralized product by addition of a liquid binder as described in Japanese Patent Laid-Open No. Hei 3-33199; and the like.

In addition, there can be employed a process described in Japanese Patent Laid-Open No. Hei 10-176200, comprising granulating a mixture comprising a nonionic surfactant, an acid precursor of an anionic surfactant capable of having a lamellar orientation, and a mixture of alkalizing agents, while tumbling with an agitator-granulator at a temperature not less than the temperature capable of neutralizing the mixture, and the like.

In addition, there can be included a step of separating with a sieve or the like particles having a particle size equal to or larger than that required (coarse grains) contained in the detergent particles obtained by the above-mentioned operations, and the separated coarse grains are disintegrated into a smaller particle size and can be used as the detergent particles. The disintegrators of the coarse grains include impact disruptors such as hammer crushers; impact pulverizers such as atomizers and pin-mills; shearing rough pulverizers such as flash mills; and the like. These disintegrators can be carried out in a single-step operation, or in a multi-step operation with the same or different pulverizers. In this case, it is preferable that a fine powder is added as an agent for suppressing deposition in the device or a treatment agent for modifying a pulverized surface. The fine powder is preferable inorganic powders of aluminosilicates, silicon dioxide, bentonite, talc, clay, amorphous silica derivatives, and the like, and

especially crystalline or amorphous aluminosilicates are preferable. In addition, fine powders of water-soluble substances such as sodium carbonate, sodium sulfate, and sodium tripolyphosphates can be also used.

In addition, for the purposes of fixing and smoothing of a surface-modifying agent in order to improve the flowability of the particles subjected to the disintegration treatment, there can be provided a surface-modifying step. For instance, this process comprises supplying a composition into a rotary cylindrical mixer or agitator in a batch or continuous process, and treating the composition with tumbling or agitation.

#### 4. Composite Detergent Particles

The composite detergent particles of the present invention are prepared by dry-blending the detergent additive particles (a) and the detergent particles (b) mentioned above. By dry-blending the detergent additive particles (a), the resulting composite detergent particles have excellent distributivity from the dispenser, and by dry-blending the detergent particles (b), the composite detergent particles have excellent detergency. Specifically, a continuous paste layer comprising a high-concentration surfactant formed by the detergent particles (b) can be rapidly made discontinuous by mixing with the detergent additive particles (a) having a specified composition and specified powder properties and fast dissolubility upon pouring water into the dispenser. Further, the composite detergent particles can be rapidly and efficiently distributed in the dispenser by the actions of discontinuity together with an action of the fast dissolution of the detergent additive particles (a) upon pouring water. From the viewpoints of exhibiting a more excellent distributivity of the composite



detergent particles from the dispenser and a more excellent detergency, the preferred mixing ratio of the detergent additive particles (a) to the detergent particles (b), as expressed by the weight ratio of (a)/(b), is preferably from 1/99 to 70/30, more preferably from 2/98 to 60/40, still more preferably from 3/97 to 55/45, still more preferably from 5/95 to 50/50, still more preferably from 10/90 to 45/55, still more preferably from 15/85 to 40/60, most preferably from 20/80 to 35/65.

Here, as to the extent of dry-blending of the detergent additive particles (a) and the detergent particles (b), some effects of improving the distributivity from the dispenser are exhibited even if the extent of blending is low. However, from the viewpoints of constantly exhibiting the effect of improving the distributivity and being capable of efficiently making the formed paste layer comprising a surfactant discontinuous upon pouring water by mixing with the detergent additive particles (a), the higher the extent of dry-blending, the better. For instance, when an extent of dry-blending is expressed by the difference of the surfactant content of an about 20 gram sample collected arbitrarily at two sites in the composite detergent particles and/or the granular detergent composition comprising the composite detergent particles, the difference in the surfactant content is preferably within 7%, more preferably within 5%, still more preferably within 3%, most preferably within 1%.

In addition, as the process of dry-blending, those blending processes in a batch or continuous process with V-type blender, and the like can be employed.

## 5. Granular Detergent Composition

The granular detergent composition of the present invention comprises 50

to 100% by weight of the composite detergent particles mentioned above, and the granular detergent composition has excellent distributivity from the dispenser. In addition, the preferred content of the composite detergent particles is 60% by weight or more, more preferably 70% by weight or more, still more preferably 80% by weight or more, still more preferably 85% by weight or more, still more preferably 90% by weight or more, most preferably 95% by weight or more, from the viewpoint of further reflecting the excellent distributivity from the dispenser owned by the composite detergent particles to the detergent composition.

In addition, the preferred content of the detergent additive particles (a) in the granular detergent composition is preferably from 1 to 70% by weight, more preferably from 2 to 60% by weight, still more preferably from 3 to 55% by weight, still more preferably from 5 to 50% by weight, still more preferably from 10 to 45% by weight, still more preferably from 15 to 40% by weight, most preferably from 20 to 35% by weight, from the viewpoints of satisfying both the distributivity from the dispenser and the detergency.

Also, in the granular detergent composition of the present invention having improved distributivity from the dispenser by the inclusion of the detergent additive particles (a), there can be properly formulated components such as bleaching agents such as percarbonates and foamable percarbonates; granular crystalline silicates; bleaching activators such as compounds listed in Japanese Patent Laid-Open No. Hei 6-316700 and tetraacetyl ethylenediamine; enzymes such as protease, cellulase, amylase and lipase; biphenyl-type or stilbene-type fluorescent dyes; silicone/silica-based defoaming agents; antioxidants; blueing agents; perfumes, and/or particles including these

components, regardless of the fastness of the dissolving rate of the particles.

## EXAMPLES

### [Preparation of Detergent Additive Particles (a)]

5           Detergent Additive Particles 1 of the present invention were prepared by the process described below.

10           Four-hundred and fifteen kilograms of water was added to a 1 m<sup>3</sup>-mixing vessel having agitation impellers, and the water temperature was adjusted to 50°C. One-hundred and thirty-five kilograms of sodium sulfate, 115 kg of sodium carbonate, and 100 kg of a 40% by weight-aqueous sodium polyacrylate solution were added thereto. Further, the resulting mixture was agitated for 15 minutes with temperature-controlled to 50°C, and thereafter 185 kg of zeolite was added thereto. The resulting mixture was further agitated for 30 minutes with temperature-controlled to 50°C, to give a homogeneous slurry.

15           This slurry was supplied to a spray-drying tower with a pump, and sprayed with a pressure spray nozzle arranged near the top of the tower at a spraying pressure of 25 kg/cm<sup>2</sup>. A high-temperature gas fed to the spray-drying tower was supplied from the lower portion of the tower at a temperature of 220°C and exhausted from the top of the tower at 103°C. Subsequently, coarse  
20           detergent additive particles obtained from the lower part of the tower were dried with a hot air at 100°C in a fluidized bed until the water content attained to 5% by weight. Coarse grains of the resulting particles were removed with a 1410 µm-sieve, to give Detergent Additive Particles 1. The composition and the properties of the resulting Particles 1 are shown in Table 1.

25           Incidentally, the microporous capacity at 0.01 to 4 µm was 0.40 mL/g, as

determined by a mercury porosimeter for Detergent Additive Particles 1. In addition, the dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 92% of the particles. (Incidentally, an average value for size of released bubbles/particle size in the above 92% of the particles was 5.8/10.) In addition, Detergent Additive Particles 1 were analyzed for a cave-in hole. As a result, the particles were composed of 82% of cave-in particles, in which a hole having a projected area diameter of 2% or more and a depth of 10% or more, of a projected area diameter of the particle was present at one or more points. In addition, the average of

$$\frac{\text{projected area diameter of hole}}{\text{projected area diameter of particle}} \times 100$$

of a cave-in hole for the 82% of cave-in particles was 22%. In addition, the average depth of the cave-in hole was 50% of the projected area diameter of the particle. In addition, as a result of analyses of Detergent Additive Particles 1 by FT-IR/PAS and EDS, it was confirmed that the particles had a localized structure in which a higher proportion of zeolite was present in the inner portion of the particle, and higher proportions of the polymer and the water-soluble inorganic salt, which are the water-soluble substances, were present near the particle surface.

Detergent Additive Particles 2 of the present invention were prepared by the process described below.

Thirty-hundred and ninety kilograms of water was added to a 1 m<sup>3</sup>-mixing vessel having agitation impellers, and the water temperature was adjusted to 50°C. Fifty kilograms of a 50% by weight-aqueous sodium alkylbenzenesulfonate solution was added thereto. The resulting mixture was agitated for 15 minutes, and thereafter, 125 kg of sodium sulfate, 110 kg of sodium carbonate, and 100 kg of a 40% by weight-aqueous sodium polyacrylate solution were added thereto. After agitating the resulting mixture for additional 15 minutes with temperature-controlled to 50°C, 175 kg of zeolite was added thereto. The resulting mixture was further agitated for 30 minutes with temperature-controlled to 50°C, to give a homogeneous slurry.

This slurry was supplied to a spray-drying tower with a pump, and sprayed with a pressure spray nozzle arranged near the top of the tower at a spraying pressure of 25 kg/cm<sup>2</sup>. A high-temperature gas fed to the spray-drying tower was supplied from the lower portion of the tower at a temperature of 218°C and exhausted from the top of the tower at 101°C. Subsequently, coarse detergent additive particles obtained from the lower part of the tower were dried with a hot air at 100°C in a fluidized bed until the water content attained to 5% by weight. Coarse grains of the resulting particles were removed with a 1410 µm-sieve, to give Detergent Additive Particles 2. The composition and the properties of the resulting Particles 2 are shown in Table 1.

Incidentally, the microporous capacity at 0.01 to 4 µm was 0.44 mL/g, as determined by a mercury porosimeter. In addition, its dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 88% of the particles. (Incidentally, an average value for size of released bubbles/particle

size in the above 88% of the particles was 6.0/10.) In addition, Detergent Additive Particles 2 were analyzed for a cave-in hole. As a result, the particles were composed of 11% of cave-in particles, in which a hole having a projected area diameter of 2% or more and a depth of 10% or more of a projected area diameter of the particle was present at one or more points. In addition, the average of

$$\frac{\text{projected area diameter of hole}}{\text{projected area diameter of particle}} \times 100$$

of a cave-in hole for the 11% of cave-in particles was 14%. In addition, the average depth of the cave-in hole was 61% of the projected area diameter of the particle. In addition, as a result of analyses of Detergent Additive Particles 2 by FT-IR/PAS and EDS, it was confirmed that the particles also had a localized structure, as in Detergent Additive Particles 1.

Detergent Additive Particles 3 of the present invention were prepared by the process described below.

Four-hundred and sixteen kilograms of water was added to a 1 m<sup>3</sup>-mixing vessel having agitation impellers, and the water temperature was adjusted to 50°C. Two-hundred and forty-eight kilograms of sodium sulfate, 92 kg of sodium carbonate, and 100 kg of a 40% by weight-aqueous sodium polyacrylate solution were added thereto. Further, the resulting mixture was agitated for 30 minutes with temperature-controlled to 50°C, to give a homogeneous slurry.

This slurry was supplied to a spray-drying tower with a pump, and sprayed with a pressure spray nozzle arranged near the top of the tower at a spraying pressure of 25 kg/cm<sup>2</sup>. A high-temperature gas fed to the spray-drying tower was supplied from the lower portion of the tower at a temperature of 228°C and exhausted from the top of the tower at 100°C. Subsequently, coarse detergent additive particles obtained from the lower part of the tower were dried with a hot air at 100°C in a fluidized bed until the water content attained to 5% by weight. Coarse grains of the resulting particles were removed with a 1410 µm-sieve, to give Detergent Additive Particles 3. The composition and the properties of the resulting Particles 3 are shown in Table 1.

Incidentally, the microporous capacity at 0.01 to 4 µm was 0.50 mL/g, as determined by a mercury porosimeter. In addition, the dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 90% of the particles. (Incidentally, an average value for size of released bubbles/particle size in the above 90% of the particles was 6.3/10.) In addition, Detergent Additive Particles 3 were analyzed for a cave-in hole. As a result, the particles were composed of 27% of cave-in particles, in which a hole having a projected area diameter of 2% or more and a depth of 10% or more of a projected area diameter of the particle was present at one or more points. In addition, the average of

$$\frac{\text{projected area diameter of hole}}{\text{projected area diameter of particle}} \times 100$$

of a cave-in hole for the 27% of cave-in particles was 18%. In addition, the average depth of the cave-in hole was 68% of the projected area diameter of the particle. In addition, as a result of analyses of Detergent Additive Particles 3 by FT-IR/PAS and EDS, it was confirmed that the particles had a localized structure in which a lower proportion of the polymer was present in the inner portion of the particle, and a higher proportion of the polymer was present near the particle surface.

Detergent Additive Particles 4 of the present invention were prepared by the process described below.

A 4% by weight polyoxyethylene alkyl ether as listed in Table 1 was heated to 60°C. Next, 96% by weight of Detergent Additive Particles 1 were supplied into Lödige Mixer (manufactured by Matsuzaka Giken Co., Ltd.; capacity: 20 L; equipped with a jacket), and agitations of a main shaft (150 rpm) and a chopper (4000 rpm) were initiated. Incidentally, the jacket was heated to 60°C. The above polyoxyethylene alkyl ether was supplied into the above mixer in 30 seconds, and thereafter the components were agitated for 4 minutes, to give Detergent Additive Particles 4. The composition and the properties of the resulting Particles 4 are shown in Table 1.

Incidentally, the microporous capacity at 0.01 to 4  $\mu\text{m}$  was 0.38 mL/g, as determined by a mercury porosimeter. In addition, the dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 89% of the particles. (Incidentally, an average value for size of released bubbles/particle size in the above 89% of the particles was 5.8/10.) In addition, Detergent



Additive Particles 4 were analyzed for a cave-in hole. As a result, the particles were composed of 80% of cave-in particles, in which a hole having a projected area diameter of 2% or more and a depth of 10% or more of a projected area diameter of the particle was present at one or more points. In addition, the average of

$$\frac{\text{projected area diameter of hole}}{\text{projected area diameter of particle}} \times 100$$

of a cave-in hole for the 80% of cave-in particles was 21%. In addition, the average depth of the cave-in hole was 49% of the projected area diameter of the particle. In addition, as a result of analyses of Detergent Additive Particles 4 by FT-IR/PAS and EDS, it was confirmed that the particles also had a localized structure, as in Detergent Additive Particles 1.

Detergent Additive Particles 5 of the present invention were prepared by the process described below.

A batch kneader equipped with a jacket was heated to 50°C, and charged with 24.9 kg water. Thereto were added 8.1 kg of sodium sulfate, 6.9 kg of sodium carbonate, and 6 kg of a 40% by weight-aqueous sodium polyacrylate solution. Further, the resulting mixture was agitated for 15 minutes with temperature-controlled to 50°C, and thereafter 11.1 kg of zeolite was added thereto. The resulting mixture was further agitated for 30 minutes with temperature-controlled to 50°C. Thereafter, the temperature of the jacket was heated to 80°C, and at the same time the pressure inside the mixing vessel of the

batch kneader was reduced, thereby drying the components with mixing until the water content attained to 5% by weight. Coarse grains of the resulting particles were removed with a 500  $\mu\text{m}$ -sieve, to give Detergent Additive Particles 5. The composition and the properties of Particles 5 are shown in Table 1.

5           Incidentally, the microporous capacity at 0.01 to 4  $\mu\text{m}$  was 0.21 mL/g, as determined by a mercury porosimeter. In addition, the dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 9% of the particles. (Incidentally, an average value for size of released bubbles/particle size in the above 9% of the particles was 1.7/10.) In addition, Detergent Additive Particles 5 were analyzed for a cave-in hole. As a result, there was confirmed no cave-in particle in which a hole having a projected area diameter of 2% or more and a depth of 10% or more of a projected area diameter of the particle was present at one or more points. In addition, as a result of analyses of Detergent Additive Particles 5 by FT-IR/PAS and EDS, a definite localized structure was not found.

Comparative Particles 1, a comparative example of the present invention, were prepared by the process described below.

20           A 347.5 kg water was added to a 1 m<sup>3</sup>-mixing vessel having agitation impellers. The water temperature was adjusted to 50°C, and 150 kg of a 50% by weight-aqueous sodium alkylbenzenesulfonate solution was added thereto. After agitating the resulting mixture for 15 minutes, 115 kg of sodium sulfate, 100 kg of sodium carbonate, and 87.5 kg of a 40% by weight-aqueous sodium polyacrylate solution were added thereto. The resulting mixture was agitated for

additional 15 minutes with temperature-controlled to 50°C, and thereafter 150 kg of zeolite was added thereto. The resulting mixture was further agitated for 30 minutes with temperature-controlled to 50°C, to give a homogeneous slurry.

This slurry was supplied to a spray-drying tower with a pump, and sprayed with a pressure spray nozzle arranged near the top of the tower at a spraying pressure of 25 kg/cm<sup>2</sup>. A high-temperature gas fed to the spray-drying tower was supplied from the lower portion of the tower at a temperature of 222°C and exhausted from the top of the tower at 105°C. Subsequently, particles obtained from the lower part of the tower was dried with a hot air at 100°C in a fluidized bed until the water content attained to 5% by weight. Coarse grains of the resulting particles were removed with a 1410 µm-sieve, to give Comparative Particles 1. The composition and the properties of Comparative Particles 1 are shown in Table 1.

Incidentally, the microporous capacity at 0.01 to 4 µm was 0.43 mL/g, as determined by a mercury porosimeter. In addition, the dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 85% of the particles. (Incidentally, an average value for size of released bubbles/particle size in the above 85% of the particles was 6.2/10.) In addition, Comparative Particles 1 were analyzed for a cave-in hole. As a result, the particles were composed of 8% of cave-in particles, in which a hole having a projected area diameter of 2% or more and a depth of 10% or more of a projected area diameter of the particle was present at one or more points. In addition, the average of

$$\frac{\text{projected area diameter of hole}}{\text{projected area diameter of particle}} \times 100$$

of a cave-in hole for the 8% of cave-in particles was 10%. In addition, the average depth of the cave-in hole was 65% of the projected area diameter of the particle. In addition, as a result of analyses of Comparative Particles 1 by FT-IR/PAS and EDS, it was confirmed that the particles had a localized structure in which a higher proportion of zeolite was present in the inner portion of the particle, and higher proportions of the polymer and the water-soluble inorganic salt, which are the water-soluble substances, were present near the particle surface.

Comparative Particles 2, a comparative example of the present invention, were prepared by the process described below.

A batch kneader equipped with a jacket was heated to 50°C, and charged with 20.85 kg water, and 9 kg of a 50% by weight-aqueous sodium alkylbenzenesulfonate solution was added thereto. After agitating the resulting mixture for 15 minutes, 6.9 kg of sodium sulfate, 6 kg of sodium carbonate, and 5.25 kg of a 40% by weight-aqueous sodium polyacrylate solution were added thereto. The resulting mixture was agitated for additional 15 minutes with temperature-controlled to 50°C, and thereafter 9 kg of zeolite was added thereto. The resulting mixture was further agitated for 30 minutes with temperature-controlled to 50°C. Thereafter, the temperature of the jacket was heated to 80°C, and at the same time the pressure inside the mixing vessel of the batch kneader

was reduced, thereby drying the components until the water content attained to 5% by weight. Coarse grains of the resulting particles were removed with a 1000  $\mu\text{m}$ -sieve, to give Comparative Particles 2. The composition and the properties of Comparative Particles 2 are shown in Table 1.

Incidentally, the microporous capacity at 0.01 to 4  $\mu\text{m}$  was 0.19 mL/g, as determined by a mercury porosimeter. In addition, the dissolution behavior was observed by a digital microscope. As a result, it was confirmed that bubbles having a size of 1/10 or more of the particle size were released from 8% of the particles. (Incidentally, an average value for size of released bubbles/particle size in the above 8% of the particles was 1.6/10.) In addition, Comparative Particles 2 were analyzed for a cave-in hole. As a result, there was confirmed no cave-in particle in which a hole having a projected area diameter of 2% or more and a depth of 10% or more of a projected area diameter of a particle was present at one or more points. In addition, as a result of analyses of Comparative Particles 2 by FT-IR/PAS and EDS, as definite localized structure was not found.

As Comparative Particles 3, a comparative example of the present invention, sodium carbonate particles (DENSE ASH: manufactured by Central Glass Co., Ltd.) were used. As Comparative Particles 4, sodium percarbonate granular particles (KCPZ: manufactured by Nippon Peroxide K.K.) were used. As Comparative Particles 5, enzyme granular particles (Savinase 18T Type W: manufactured by NOVO Nordisk) were used. The composition and the properties of each group of Comparative Particles 3 to 5 are shown in Table 1.

Table 1

	Detergent Additive Particles					Comparative Particles				
	1	2	3	4	5	1	2	3	4	5
<u>Formulating Composition</u> (% by weight)										
LAS-Na <sup>1)</sup>		5				15	15			
Polyoxyethylene Alkyl Ether <sup>2)</sup>				4						
Sodium Carbonate <sup>3)</sup>	23	22	23	22	23	20	20	100		
Sodium Sulfate <sup>4)</sup>	27	25	62	26	27	23	23			
Sodium Polyacrylate <sup>5)</sup>	8	8	10	8	8	7	7			
Zeolite <sup>6)</sup>	37	35		35	37	30	30			
Water	5	5	5	5	5	5	5			
Sodium Percarbonate Granule									100	
Enzyme Granule										100

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	Detergent Additive Particles					Comparative Particles				
	1	2	3	4	5	1	2	3	4	5
<u>Properties</u>										
Bulk Density (g/L)	570	540	475	575	760	465	780	1070	800	1150
Average Particle Size ( $\mu\text{m}$ )	280	275	288	285	220	302	380	290	510	552
Dissolution Rate (%) at 5°C after 60 seconds	99	96	99	98	91	90	78	99	60	66
Microporous Capacity (mL/g)	0.4	0.44	0.5	0.38	0.21	0.43	0.19	0.05	0.12	0.04
Ratio of Bubble Generation (%)	92	88	90	89	9	85	8	0	0	0
Ratio of Cave-in Particle (%)	82	11	27	80	0	8	0	0	0	0
Localized Structure	Yes	Yes	Yes	Yes	No	Yes	No	No	Yes	Yes

- 1): NEOPELEX F65 (manufactured by Kao Corporation)
- 2): EMULGEN 108 KM, average moles of ethylene oxides: 8.5 (manufactured by Kao Corporation)
- 3): DENSE ASH (manufactured by Central Glass Co., Ltd.)
- 4): Anhydrous neutral sodium sulfate (manufactured by Shikoku Kasei K.K.)
- 5): Average molecular weight: 10000
- 6): Zeolite 4A-type, average particle size: 3.5  $\mu\text{m}$  (manufactured by Tosoh Corporation)

[Preparation of Detergent Particles (b)]

Detergent Particles 1 were prepared by the process described below.

5 A slurry having a water content of 48%, comprising components of each ingredient for Detergent Particles 1 listed in Table 2 except for 50% by weight of the formulated amount of polyoxyethylene alkyl ether, the entire formulated amount of a crystalline silicate, and 50% by weight of the formulated amount of zeolite, was spray-dried to give spray-dried base material having a bulk density of 310 g/L. Next, the spray-dried base material was supplied into High-Speed Mixer (manufactured by Fukae Powtec Corp., agitation tumbling granulator, equipped with a jacket), and 20% by weight of the formulated amount of the zeolite, and the entire amount of the crystalline silicate were added thereto. The remaining 50% by weight of the formulated amount of the polyoxyethylene alkyl ether heated to 70°C was added by spraying, and the mixture was granulated. Further, the resulting granular product was surface-treated by adding 20% by weight of the formulated amount of the zeolite 60 seconds before the termination of the granulation, to give a granule. Further, the granule was classified with a sieve having a sieve-opening of 1410  $\mu\text{m}$ , and the remaining 10% by weight of the zeolite was added to coarse grains having a size of 1410  $\mu\text{m}$  or more. The resulting mixture was pulverized by Fitz Mill (pulverizer, manufactured by Hosokawa Micron Corporation) to a size of 1410  $\mu\text{m}$  or less, and thereafter the pulverized product was mixed with the sieve-passed granule, to give Detergent Particles 1.

Detergent Particles 2 were prepared by the process described below.

25 A slurry having a water content of 48%, comprising components of each



ingredient for Detergent Particles 2 listed in Table 2 except for 50% by weight of the formulated amount of polyoxyethylene alkyl ether, the entire formulated amount of a crystalline silicate, and 50% by weight of the formulated amount of zeolite, was spray-dried to give spray-dried base material having a bulk density of 302 g/L. Next, the spray-dried base material was supplied into High-Speed Mixer (manufactured by Fukae Powtec Corp., agitation tumbling granulator, equipped with a jacket), and 20% by weight of the formulated amount of the zeolite, and the entire amount of the crystalline silicate were added thereto. The remaining 50% by weight of the formulated amount of the polyoxyethylene alkyl ether heated to 70°C was added by spraying, and the mixture was granulated. Further, the resulting granular product was surface-treated by adding 20% by weight of the formulated amount of the zeolite 60 seconds before the termination of the granulation, to give a granule. Further, the granule was subjected to the same treatment as in Detergent Particles 1, to give Detergent Particles 2.

Detergent Particles 3 were prepared by the method described below.

A slurry having a water content of 50%, comprising the entire formulated amount of each of sodium polyacrylate, PEG, sodium sulfate, sodium sulfite, a soap and a fluorescent dye, 50% by weight of the formulated amount of zeolite, and 50% by weight of the formulated amount of sodium carbonate, was spray-dried to give spray-dried base material having a bulk density of 460 g/L. The resulting spray-dried base material, the entire formulated amounts of an amorphous aluminosilicate and a crystalline silicate, and the remaining 50% by weight of the formulated amount of sodium carbonate were supplied into Lödige Mixer, and the agitation was initiated. Heated water at 40°C was allowed to flow

through the jacket. The entire formulated amount of the polyoxyethylene alkyl ether heated to 70°C was added by spraying, and the mixture was granulated. Further, the resulting granular product was surface-treated by adding 30% by weight of the formulated amount of the zeolite at the time 60 seconds before the termination of the granulation, to give a granule. The resulting granule was classified with a sieve having a sieve-opening of 1410  $\mu\text{m}$ , and 20% by weight of the formulated amount of the zeolite was added to coarse grains having a size of 1410  $\mu\text{m}$  or more. The resulting mixture was pulverized by a pulverizer (pulverizer, manufactured by Hosokawa Micron Corporation), and thereafter the pulverized product was mixed with the sieve-passed product, to give Detergent Particles 3.

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Table 2

	Detergent Particles		
	1	2	3
<u>Formulating Composition</u>			
<u>(% by weight)</u>			
LAS-Na <sup>1)</sup>	23	25.6	
AS-Na <sup>7)</sup>	7	7.8	
Polyoxyethylene Alkyl Ether <sup>2)</sup>	4	4.4	20
Soap <sup>8)</sup>	3	3.3	5
PEG <sup>9)</sup>	2	2.2	2
No. 1 Sodium Silicate <sup>10)</sup>	10	11.1	
Crystalline Silicate <sup>11)</sup>	5	5.6	24
Zeolite <sup>6)</sup>	25	23.7	18
Amorphous Aluminosilicate <sup>12)</sup>			10
Sodium Carbonate <sup>3)</sup>	9	7.4	10
Sodium Sulfate <sup>4)</sup>	3	0.3	3
Sodium Sulfite <sup>13)</sup>	0.5	0.6	0.5
Sodium Polyacrylate <sup>5)</sup>	3	2.4	5
Fluorescent Dye <sup>14)</sup>	0.5	0.6	0.5
Water	5	5	2
<u>Properties</u>			
Bulk Density (g/L)	785	776	820
Average Particle Size (μm)	394	412	355

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1) to 6) are the same as in Table 1.

7): Alkylsulfate having 12 to 18 carbon atoms

8): Sodium salt of fatty acid of beef tallow (14 to 18 carbon atoms)

9): Polyethylene glycol (average molecular weight: 10000)

5 10): No. 1 sodium silicate (manufactured by Tosoh Corporation,  
solid content: 44% by weight)

11): Product prepared by pulverizing SKS-6 (manufactured by Clariant  
Tokuyama, average particle size: 120  $\mu\text{m}$ ) by a roll mill (average  
particle size: 8  $\mu\text{m}$ )

10 12): Product described in Preparation Example 2 of Japanese Patent Laid-Open  
No. Hei 9-132794 (average particle size: 8  $\mu\text{m}$ )

13): Sodium Sulfite (manufactured by Mitsui Toatsu K.K.)

14): Mixture of Tinopal CBS-X and Tinopal AMS-GX (manufactured by Ciba  
Specialty Chemicals K.K.) in the weight ratio of 1:1

15  
20 Subsequently, each group of Detergent Additive Particles 1 to 5 of the  
present invention and Comparative Particles 1 to 5 was dry-blended with each  
group of Detergent Particles 1 to 3 for 5 minutes in a V-blender in a weight ratio  
of 5/95, 10/90 or 30/70, thereby giving composite detergent particles of the  
present invention and composite detergent particles of comparative examples.

25 Further, based on 99 parts by weight of each group of the above Detergent  
Particles 1 to 3 and the above composite detergent particles, 1 part by weight of  
enzyme granules [0.4 parts by weight of a cellulase ("KAC500," manufactured  
by Kao Corporation), 0.3 parts by weight of a protease ("Savinase 12.0T-W,"  
manufactured by NOVO Nordisk), and 0.3 parts by weight of a lipase ("Lipolase

100T," manufactured by NOVO Nordisk)] were additionally added, and the resulting mixture was dry-blended for 5 minutes in the V-blender, to give a granular detergent composition of the present invention and a granular detergent composition of a comparative example.

5           The granular detergent compositions obtained as above were evaluated for the distributivity in a dispenser of a drum-type washing machine by the following method.

[Evaluation of Distributivity in Dispenser]

10           Twenty grams of a granular detergent composition was placed in a dried detergent-supplying case of a drum-type washing machine "ES-E60," manufactured by Sharp Corporation, and tap water at 20°C was poured into an empty drum. After pouring water was ended, the granular detergent composition remaining in the detergent-supplying case was recovered. The weight of the  
15           composition after drying at 105°C for 4 hours was measured, and the remaining ratio was calculated by the following equation (4).

$$\text{Remaining Ratio (\%)} = 100 \times \frac{(\text{Dry Weight of Residue (g)})}{20 \text{ (g)}} \quad (4)$$

20           The results of the evaluation (remaining ratios) of each of the granular detergent compositions in which the detergent additive particles of the present invention were mixed, and the compositions of Comparative Examples are shown in Table 3.

Table 3

(Detergent Additive Particles or Comparative Particles)/  
Detergent Particles = 0/100 (weight ratio)

Comparative Example	
Detergent Particles 1	53%
Detergent Particles 2	58%
Detergent Particles 3	62%

(Detergent Additive Particles or Comparative Particles)/Detergent Particles =  
5/95 (weight ratio)

	Example Additive Particles 1	Example Additive Particles 2	Example Additive Particles 3	Example Additive Particles 4	Example Additive Particles 5
Detergent Particles 1	2%	8%	0%	7%	18%
Detergent Particles 2	3%	6%	0%	5%	14%
Detergent Particles 3	3%	6%	0%	9%	17%

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	Comp. Ex. Comp. Particles 1	Comp. Ex. Comp. Particles 2	Comp. Ex. Comp. Particles 3	Comp. Ex. Comp. Particles 4	Comp. Ex. Comp. Particles 5
Detergent Particles 1	46%	53%	64%	66%	56%
Detergent Particles 2	41%	56%	60%	62%	57%
Detergent Particles 3	47%	61%	63%	70%	62%

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(Detergent Additive Particles or Comparative Particles)/Detergent Particles =  
10/90 (weight ratio)

	Example Additive Particles 1	Example Additive Particles 2	Example Additive Particles 3	Example Additive Particles 4	Example Additive Particles 5
Detergent Particles 1	0%	2%	0%	1%	9%
Detergent Particles 2	0%	1%	0%	0%	10%
Detergent Particles 3	0%	2%	0%	3%	6%

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	Comp. Ex. Comp. Particles 1	Comp. Ex. Comp. Particles 2	Comp. Ex. Comp. Particles 3	Comp. Ex. Comp. Particles 4	Comp. Ex. Comp. Particles 5
Detergent Particles 1	39%	50%	68%	68%	58%
Detergent Particles 2	40%	52%	61%	67%	58%
Detergent Particles 3	44%	55%	66%	69%	60%

(Detergent Additive Particles or Comparative Particles)/Detergent Particles =  
30/70 (weight ratio)

	Example Additive Particles 1	Example Additive Particles 2	Example Additive Particles 3	Example Additive Particles 4	Example Additive Particles 5
Detergent Particles 1	0%	0%	0%	0%	2%
Detergent Particles 2	0%	0%	0%	0%	0%
Detergent Particles 3	0%	0%	0%	0%	2%

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	Comp. Ex. Comp. Particles 1	Comp. Ex. Comp. Particles 2	Comp. Ex. Comp. Particles 3	Comp. Ex. Comp. Particles 4	Comp. Ex. Comp. Particles 5
Detergent Particles 1	32%	49%	55%	62%	53%
Detergent Particles 2	29%	47%	63%	65%	55%
Detergent Particles 3	27%	50%	67%	63%	56%

It is clear from the results shown in Table 3 that each of the granular detergent composition, in which the detergent additive particles of the present invention were mixed, has markedly excellent distributivity as compared with those of Comparative Examples.

In addition, each group of the composite detergent particles obtained by dry-blending Detergent Additive Particles 1 and Detergent Particle 1 in a weight ratio of 5/95, 10/90 or 30/70 for 5 minutes in a V-blender was subjected to a classification test by transportation. As a result, the classification of the detergent additive particles was not found.

#### INDUSTRIAL APPLICABILITY

The detergent additive particles of the present invention have an effect of enhancing the distributivity of the granular detergent composition in running water prepared by mixing the detergent additive particles with the detergent particle. In the case where the granular detergent composition is supplied by using a dispenser attached to a washing machine such as a drum-type washing machine, in addition to its excellent distributivity in the washing machine,



troubles that the granular detergent composition forms an aggregate and remains in the dispenser are improved.

5 The present invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

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